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16. ABSTRACT

The Environmental Monitoring Systems Laboratory/Research Triangle Park, N. C. (EMSL/RTP) has the responsibility within EPA of developing methods of monitoring for present and future regulated pollutants. Consequently, EMSL/RTP has prepared a three-year methods development strategy in the area of methods development for air pollutants. This article addresses three major areas of concern: ambient, source, and exposure monitoring. Each of these areas is further divided into four categories: inorganic particulate matter, inorganic gases, organic particulate matter, and organic gases. The problems and needs inherent in both sampling and analysis phases are discussed.

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Air monitoring: Research needs

New sampling and analytical techniques need to be developed for ambient, source, and exposure monitoring

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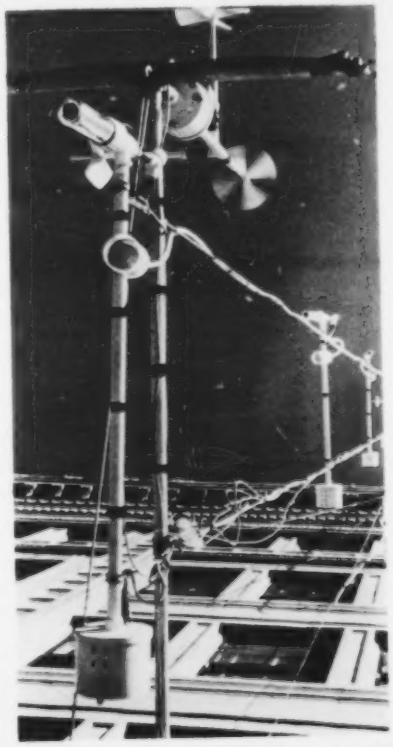
Among its many activities, the Environmental Monitoring Systems Laboratory at Research Triangle Park, N.C. (EMSL/RTP) has the responsibility within EPA to develop methods of monitoring for regulated air pollutants and for those that may be regulated in the future. These include air pollutants at the source and in the ambient air. Consequently, EMSL/RTP has prepared a three-year methods development strategy that will be used to formulate program plans and to allocate resources (both intra and extramurally) in the area of methods development for air pollutants. Essentially the strategy consists of compiling and assessing regulatory monitoring problems and needs, defining individual research tasks, and estimating the resources necessary to accomplish these tasks in the next few years. Assigning priorities to these tasks is an ongoing activity because the air pollution data needed changes as the information to develop regulatory strategies changes. Therefore, this article addresses only the current problems and needs of the regulatory monitoring community that are being assessed by EMSL/RTP for possible funding in fiscal year (FY) 1983 and FY 1984.

This article addresses three major areas of concern: ambient, source, and exposure monitoring. Each of these areas is subdivided into four categories: inorganic particulate matter, inorganic gases, organic particulate matter, and organic gases. The problems and needs inherent in both the sampling and analysis phases of the four categories are discussed.



***Closely spaced sampling inlets** provide detailed distributions of air pollutant concentrations.*

EMSL/RTP plans to conduct research in these major areas within resource limitations. Obviously, all of the research needed cannot be accomplished by EMSL scientists. In addition, because of changing budgets, time constraints, and demands on in-house expertise, it is impossible to state here which research activities will be conducted in-house and which will be conducted extramurally.

Therefore, researchers interested in working in these particular areas are invited to submit formal research proposals for review and possible funding consideration to the Office of Grants and Centers, Office of Research and Development, U.S. Environmental Protection Agency, 401 M St., S.W., Washington, D.C. 20460. A recent brochure from this office entitled "Solicitation for Research Grant Proposals" describes EPA's high-priority needs in environmental measurements (EPA 600/8-82-027, p. 15, September 1982). Applicants who prefer to discuss research plans with EPA or who wish to submit a preproposal for consideration should contact the director of EMSL/RTP (see author's address).

Background

Ambient monitoring. Any method of measuring air pollution consists of three general components: sample collection, sample analysis, and data transformation and reporting. All of these activities are important because they are interdependent, and the final result, valid data, depends upon successfully completing all three.

"Ambient air" is a very complex, dynamic system of interacting chemical species whether in the gas phase, in the particulate (solid) phase, adsorbed on the particulate phase, or in a liquid aerosol. Gaseous oxidants such as O_3 and NO_2 oxidize some organic species. Water vapor hydrolyzes both inorganic and organic gases. The surfaces of finely divided solid particles act as sites for adsorption or condensation of gaseous species. On the surfaces of these particles, reactions may occur that are catalyzed by metallic portions of the particulate matter. Photochemical reactions take place in the gas phase between reactive inorganic and/or organic species. Other photochemical reactions probably occur on the surfaces of the particles in the air. These factors introduce

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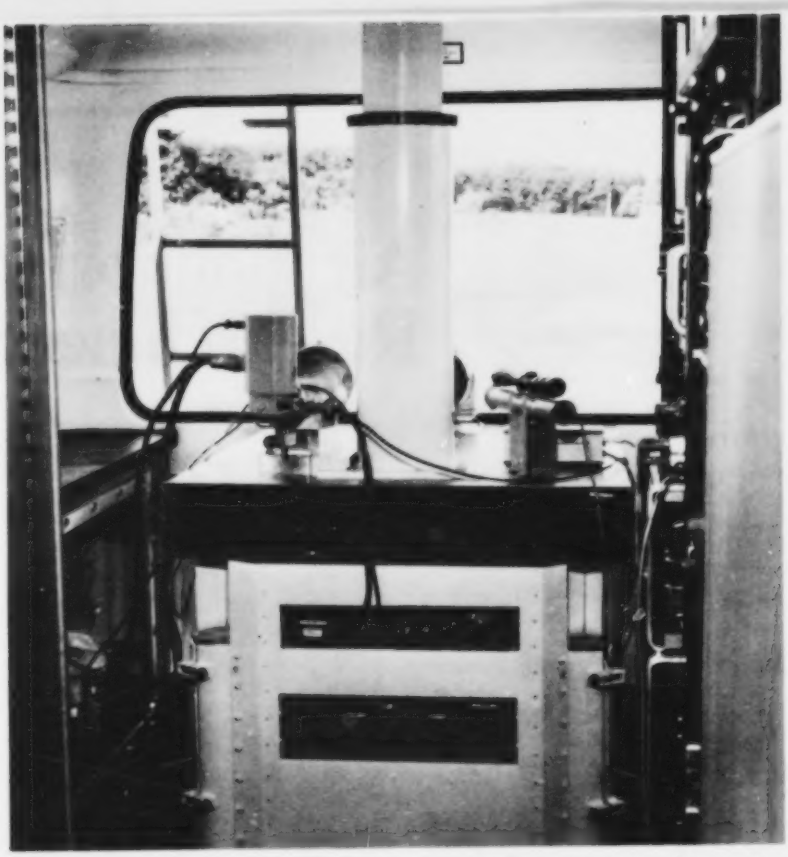
uncertainties in the determination of the actual concentrations of species existing in the ambient air at any specified time. Organic species are particularly difficult to sample and analyze because there are so many different kinds in the ambient air, and they are not necessarily stable under sampling or analysis conditions. Our present knowledge of many aspects of this complex, interacting, dynamic system is limited, particularly our understanding of the interface between gases and solid particulates.

Nearly all current sampling methods for particulate matter disturb the dynamic ambient air system. These disturbances frequently result in erroneous measurements because during sampling, new chemical species are introduced or actual ambient species are reduced. For example, some organic compounds in particulate matter collected with the high-volume air sampler interact with ozone and nitrogen oxides in the ambient air. Sampling and analysis methods must be developed that alter the chemical and physical attributes of the system as little as possible if valid data are to be produced. Optical methods are ideally suited for this purpose because the photons used as analysis probes disturb the dynamic system minimally.

The final data generated by routine operations are costly in terms of time and resources. The most efficient data reduction techniques possible must be used to ensure that maximum analytical information is obtained from raw instrumental data. Newer chemometric techniques such as factor analysis, pattern recognition, and information theory should be applied to the analytical data. Since the primary product of the laboratory is information (mainly data), the best possible methods of extracting and processing this information must be used.

Specific problems associated with ambient air will be discussed under the general categories of inorganic particulate matter, inorganic gases, organic particulate matter, and organic gases. Each category will be subdivided into discussions on sampling and analysis as applicable.

Source monitoring. Test methods for stationary sources tend to be specific for each industry and have more limited application and a smaller number of users than methods to test ambient air. EPA has proposed or promulgated 37 Reference Test Methods in support of New Source Performance Standards (NSPS), 11 in support of National Emission Standards for Hazardous Air Pollutants (NESHAP), and 4 in support of continuous emissions monitoring regulations. The large number of sources that are regulated and the pressing need for validated test methods to support these regulations have resulted in the development of test methods for stationary sources at a much faster rate than those for ambient air.



***Tunable lasers** offer advantages that are important for remote sensing and for in-situ monitoring of air pollution.*

EPA has now succeeded in controlling many of the major emitters of air pollutants, but several additional industries such as the synthetic organic chemical manufacturing industry are now being considered for regulation. However, even for these major emission sources, standardization and validation efforts still have not been completed. The needs of the agency in these areas are still great, but they are significantly different from those of the past and from those associated with ambient air. These differences result because methods for testing sources are unique in the following ways:

- First, the methods tend to require more manpower and resources than those for ambient air.
- Second, the measurements are taken over a short period of time, and because pollutant concentrations normally fluctuate temporally and spatially, sequential samples cannot be considered true replicates.
- Third, establishing the true concentration or emission rate almost always requires ancillary measurements. For example, to compensate for nonhomogeneous distribution, particulate matter almost always must be sampled at many points across the stack. Also, most test methods require measurement of one or more of the following parameters: stack gas and feedstock volumetric flow rate; stack gas and feedstock moisture or chemical content; or stack gas moisture and molecular weight, to name just a few.
- Fourth, the test methods are industry-specific and frequently are also specific for each control device. Advances in control technology can cause a previously validated test method to no longer adequately measure the emissions from a designated source. A good example of this is EPA Method 6, which originally was promulgated and validated for power plants equipped with electrostatic precipitators and fabric filters. The applicability of Method 6 to the newly developed alkaline scrubbers (for SO_2 emissions control) has been questioned because scrubber liquor may collect in the probe and scrub SO_2 from the gas as it passes through. The possibility has also been suggested that some of the scrubber liquor reaches the impingers in the form of fine particles and inter-

feres with the analysis for sulfate. We are presently investigating this problem. Similar problems have been postulated for EPA Methods 4, 5, and 7 when applied to scrubber-equipped power plants—a type of source for which they were never validated. These are just some improvements in control technologies and process changes that have created the need to reverify a previously validated method.

Some nonvalidated, EPA-approved test methods still need further work. A number of the test methods contained in EPA-approved State Implementation Plans (SIPs) are neither standardized, clearly written, nor validated.

The agency is now considering standards to control particulate emissions in the inhalable size range. There is a pressing need to standardize particle-sizing equipment for collecting condensible as well as noncondensible aerosols. Sulfuric acid mist, hydrated hydrochloric acid, nitric acid, and polynuclear organics are examples of condensible aerosols that may require regulation. At present, standardized and validated test methods are not available for these pollutants.

There is also a need to determine whether technological advances have made it possible to simplify and improve the existing methods in relation to equipment requirements and performance, manpower and resource requirements, and applications. For example, significant cost savings will result if source test methods are made less specific for each source and each pollutant. Power plants again serve as a useful example. They have to measure carbon dioxide or oxygen, particulates, sulfur dioxide and nitrogen oxides, and may eventually have to control emissions of acid mist and toxic metals. Under today's regulations this would involve separate tests with EPA Reference Methods 3, 5, 6, 7, and 8. It may be possible to develop a single sampling train for all five pollutants and to perform the chemical analysis using only two simple analytical techniques—ion chromatography and optical emission spectroscopy.

To summarize, stationary source test methodology has a firm foundation, and the opportunity now exists to improve it and to reduce the costs of the measurements while simultaneously improving their accuracy.

The problems and needs associated with methods for specific sources will be discussed under five general categories: inorganic particulates, inorganic gases, organic particulates, organic gases, and physical parameters, such as velocity and process feed.

Exposure monitoring. Exposure to a pollutant is defined as the amount of pollutant that impinges upon a receptor. The magnitude of the exposure is determined by measuring the amount of pollutant presented to the receptor during a specified time period.

In the past decade, a number of studies have attempted to estimate exposures by using data from fixed air monitoring stations and information on the residential locations of the population. This was necessitated in part by a lack of available instruments for measuring exposure directly. Recently, however, instruments and analytical techniques have been improved to the extent that exposure studies are now possible for some pollutants. Recent studies have shown that exposure estimates based on concentrations at fixed sites are not necessarily representative of actual personal exposure (*1–3*). These results underscore how important it is to continue to develop methods for measuring exposure so that scientifically valid measures of exposure to pollutants that are a public health concern can be incorporated into revisions of the criteria documents and studies of unregulated pollutants.

Methods for measuring personal exposure differ from methods for measuring ambient air and sources in several ways. First, the sample must be collected by relatively small monitors that can be retained in a person's possession 24 h a day. Therefore, these monitors must be light, quiet, and have an electronic or chemical memory. Second, suitable techniques must also be available to analyze the chemicals in the sample. A crucial problem in estimating exposure is to gather a sufficient amount of sample for later laboratory analysis.

And finally, in many situations, the need for highly specific and accurate measurement of personal exposure is secondary to the need to determine relative amounts of exposure to a given compound or compounds. For example, it may be very important to distinguish between the relative contributions of NO_2 from gas cooking and from ambient sources. Once these relative amounts are known it may be necessary to do a more in-depth study

Personal exposure monitor *collects many different volatile organic compounds on a sorbent for subsequent laboratory analysis.*

There is a pressing need to standardize particle-sizing equipment for collecting condensible as well as noncondensible aerosols.

requiring more accurate and precise methods.

Ambient problems

Inorganic particulates. *Sampling.* Even though glass-fiber filter manufacturers have made great strides in recent years, no completely satisfactory filter material for sampling particulate matter in ambient air is yet available. An inert, hydrophobic material with uniform physical properties and consistently low trace element content is required. On glass-fiber filters, artifact chemical species may be formed, which lead to artificially high mass values (*4–6*) and to high values for sulfate and nitrate. Chemical extraction of trace elements from the particulate matter collected on glass-fiber filters may also result in extraction of trace elements from the filter material. Manufacturers have difficulty supplying filters with acceptable properties.

Teflon and other polymeric membrane filters also suffer from a variety of problems including excessive pressure drop at moderate flow rates; difficulty in handling; and negative artifacts that reputedly lead to loss of particulate mass during sampling. The polymeric filters are also expensive.

For environmental protection, ambient particles of respirable size (<10 μm) are of most concern because of their health effects. Therefore, a means of collecting particulates in specified size ranges is needed. Sampler inlets designed for collection of specific size ranges are required. Sampler inlets with cut points that are well-defined and of appropriate size have become available only recently. Wind tunnel and field studies must be used to thoroughly evaluate these sampler inlets for wind speed and loading effects. This work bears directly on the revision of the National Ambient Air Quality Standards (NAAQS) for particulate matter because the new standard will probably contain a particle-size component. The reference method promulgated with NAAQS will require this information.

The mass of particulate matter collected on each stage of existing dichotomous samplers is so small that microbalances must be used to measure it. These are not widely available in the air monitoring community. There are indications that the collected particulate matter, particularly the larger size fraction, may be partially lost from the filters of dichotomous samplers before weighing (*7*). The extent of the problem should be determined and, if significant, some solution suggested. The long-standing need for a method to measure particulate matter continuously or semicontinuously still exists.

There is a recurrent need to characterize the entire size distribution of particulate matter in ambient air at various locations in the U.S. To accomplish this requires sampling devices that separate ambient particles into several size classes from very large (~50–100 μm) to very small (~0.1–1.0 μm). Instruments for this purpose have been developed only recently and are in need of thorough evaluation. The only current means of evaluating particle sampling methods is to generate aerosols in wind tunnels. There are very few facilities available.

Analysis. Currently, most methods for analyzing trace elements and inorganic ions in collected particulate matter require chemical extraction. The extraction produces a homogeneous, liquid sample that can be analyzed in an instrument. The extractions are tedious and time-consuming, and sometimes do not dissolve all of the elements or ions of interest. Chromium is an example of an element that is incompletely extracted with present procedures. Detection limits for some elements are frequently determined by the amounts of these elements present in the filter medium.

Direct methods of analysis—that is, analysis without extraction—of particulate matter for elements or inorganic ions are possible ways to eliminate these problems. Examples are X-ray emission and neutron activation analysis, both of which are multi-element techniques. The newer single-element technique, Zeeman atomic absorption, which can be used to directly analyze solids, may be useful for direct chromium analysis. Fourier transform infrared spectroscopy may be practical for direct analysis of inorganic anions in particulate matter. More development and evaluation of direct methods should be carried out.

Urban particulate Standard Reference Material (SRM 1648) from the National Bureau of Standards is the only available reference material for trace elements in ambient particulate matter. However, some trace elements of interest are not certified in this SRM. The most readily available test materials are composed of filter materials with appropriate soluble salts deposited on them. These check standards do not even roughly approach the composition of actual particulate matter. There is a need for more readily available test materials that closely resemble the composition of particulate matter.

Measuring asbestos in ambient air presents a special problem because asbestos is composed of several different fibrous minerals. Normal elemental or ion-specific methods are not applicable. The current method, which uses electron microscopy, is expensive, requires special expertise, and is of uncertain reliability. Less demanding and more pragmatic methods must be developed before meaningful assessments of the asbestos in ambient air can be made.

Inorganic gases. *Sampling and analysis.* It is anticipated that the use of incinerators for the disposal of hazardous waste will increase markedly over the next few years. Because much of the feedstock contains organically bound chlorine—such as PCBs, chlorinated hydrocarbons, pesticides, and chlorinated solvents—the major incineration products may be chlorine, hydrochloric acid, and carbonyl chloride. Therefore, it will be necessary to monitor for these compounds in the vicinity of hazardous waste incinerators.

With curent methods of continuously monitoring for nitrogen dioxide, atmospheric concentrations are found by a difference measurement—a procedure suffering inherent variability. A continuous monitor that measures nitrogen dioxide directly and is suitable for routine monitoring situations is needed.

Differential absorption lidar *uses two laser beams to measure air pollutants in three dimensions over wide areas.*

Global levels of atmospheric carbon dioxide may be changing. These changes could lead to very serious environmental consequences. Long-term monitoring of atmospheric carbon dioxide with greater accuracy than is presently possible will be needed to determine the extent of the change. Monitoring instruments with the required accuracy have not been thoroughly evaluated; it is desirable that they produce data that can be correlated with existing long-term data. Such instruments will require carefully characterized carbon dioxide reference materials available over the long term.

Because of the requirements of the Prevention of Significant Deterioration regulation (*8*), continuous monitors with improved sensitivity and lower limits of detection are needed for sulfur dioxide, nitrogen oxides, carbon monoxide, and ozone.

Organic particulate matter. *Sampling.* The question of sample integrity with respect to the organic components of particulate matter has not been thoroughly investigated. All organic compounds, even those that are normally solids at ambient conditions, have finite vapor pressures. Frequently these are high enough for a significant portion of the compounds to be in the gaseous state at equilibrium with the solid. Because air is continuously passing through previously collected particulate during sampling, organic compounds with significant vapor pressures could be partially, or totally, lost during the sampling process.

It is also possible that organic compounds with reactive functional groups could undergo some chemical changes during sample collection due to exposure to oxygen, ozone, nitrogen oxides, or water. The problem is exacerbated by the adsorption of organic compounds on particulate matter. Such adsorption affects the solid–gas equilibrium of organic compounds and may also cause problems with the subsequent analysis. Catalytic effects on the surface of particulate matter could enhance chemical reactions of adsorbed organic molecules.

In addition, the usual time delay between sample collection and sample analysis could also contribute significantly to these problems. Sampling organic particulate matter is obviously a very complex task, and the problems related to it could cause significant errors in determining the true atmospheric levels of organic compounds with even relatively low vapor pressures. Investigations to assess the magnitude of these potential problems are badly needed. The question of sample integrity for organic particulate matter will become more important when incinerators become widely used for waste chemical disposal.

Attempts to characterize organic compounds adsorbed on particulate matter are severely limited by the need for relatively large samples. Existing samplers do not collect the required amounts. In recent years, a device for collecting large amounts (~1 g/d) of ambient particulate matter has become available. The device is designed to collect particulate matter in three size ranges—<1.7 μm, 1.7–3.5 μm, and 3.5–20 μm. The two larger size ranges are collected by impaction and the smallest size range by electrostatic precipitation. The collection characteristics of the sampler, particularly the cut points, have never been thoroughly evaluated, and the device may have particle bounce and wall loss problems. The effect of the strong electric field on the production of reactive species and their resulting interactions with the collected particulates have not been studied. There is a need to determine the collection characteristics of the device and to investigate the integrity of the sample collected.

In effect, the collection of particulate matter from ambient air is a process of isolating the solid phase of a two-phase system (organic and inorganic gases/inorganic and organic solids). However, this is accomplished by dynamic (that is, nonequilibrium) exposure of the collected solid phase to large volumes of the gas phase with which it was previously in equilibrium. To obtain a representative sample of either the gas or particle phases, a sampler should be designed that disturbs the quasi-equilibrium existing in ambient air as little as possible.

Analysis. Present knowledge of the organic composition of particulate matter is very limited because of the complexity of the sample and the lack of adequate analytical methods. Techniques for the separation and identification of potentially harmful organic compounds such as azaarenes and nitroarenes in ambient particulate matter should be investigated. The increasing use of diesel engines in automobiles increases the contribution of diesel particulates to ambient particulate matter. It is necessary to develop methods to collect and analyze the specific compounds characteristic of diesel emissions.

Because ambient particulate matter may potentially contain thousands of organic compounds, it is probably hopeless to attempt to devise a method for each individual compound. Therefore, techniques to measure classes of organic compounds, such as polynuclear aromatic hydrocarbons and chlorinated aromatic compounds, should be developed. Infrared and Raman absorption methods are candidates since the spectra involved arise from molecular vibrations that are relatively independent of the specific molecules being studied. It may be necessary to preconcentrate samples before these techniques can be used.

The application of chemometric techniques to ambient air data should be explored. For example, identifying patterns in data from Fourier transform infrared measurements by factor or cluster analysis may well be an efficient means of recognizing the presence of classes of compounds in the pollutants. There is good reason to believe that applying chemometric techniques will produce much more information from a body of analytical

Because ambient particulate matter may potentially contain thousands of organic compounds, it is probably hopeless to attempt to devise a method for each individual compound.

data than is obtained with traditional methods.

Methods of analyzing organic particulate matter directly on the filter medium are needed. Such methods would avoid chemical extraction, which is now required. Possible candidate methods are infrared and Raman reflectance spectroscopy, spark source and direct probe mass spectrometry, photoacoustic absorption spectroscopy, and molecular emission (fluoresence and phosphorescence) techniques.

There are many new analytical methods, such as triple quadrupole mass spectrometry, tunable atomic line molecular spectroscopy, and gas chromatography with new detectors (e.g., photoionization) that can be used for the semivolatile organic compounds in particulate matter. These techniques should be evaluated for possible application. There is also a great need to develop new detectors for gas chromatography and especially for high-performance liquid chromatography (HPLC); at present ultraviolet absorption and fluorescence detectors are widely used for HPLC.

Quality control materials for use in methods development, such as reference materials consisting of known amounts of organic compounds in particulate matter, are nonexistent. The best that can be done at present is to spike blank filter materials with specific amounts of organic compounds and use them as quality control materials. There is a need to devise realistic quality control materials for testing the performance of techniques that analyze organic particulate matter.

Organic gases. *Sampling.* Organic species are particularly difficult to sample in ambient air because of the large number of compounds present, their very low concentrations, and their instability under ambient conditions. Photochemical reactions are known to occur in the gas phase among reactive inorganic and organic species. Other photochemical reactions probably take place on the surfaces of the particles in the air. In the case of organic compounds, even identification of relatively unstable species can be very difficult.

Because existing analytical instruments have inadequate detection limits, organic gases normally must be concentrated during sampling. This is usually accomplished with a solid sorbent such as charcoal or Tenax. Tenax has been well studied and does have limitations. It requires a laborious cleanup procedure to control blank problems, has a short useful shelf-life after sample collection (~ one month), and has a tendency to decompose during sampling to produce acetophenone and benzaldehyde.

Since the organic gases of interest have a wide range of vapor pressures and breakthrough volumes, no one solid sorbent can simultaneously collect all of them. Sampling for volatile organic gases with low breakthrough volumes, such as vinyl chloride and chloroform, is a particularly troublesome problem with existing sorbents. Semivolatile organic gases, for example those with vapor pressures less than 1 mm Hg, may be efficiently collected, but may not be completely desorbed for analysis. More stable sorbents capable of efficiently adsorbing and desorbing a wide range of organic compounds should be developed.

There is a need to characterize the surfaces of the sampling sorbents that are used at present and to determine the important criteria for designing new sorbents. It is very inefficient to synthesize new sorbents without properly identifying the important parameters. Sampling models for solid sorbents have been based on chromatography, but the quantitative relationships between the variables important for field use have not been determined for these models. Sampling with solid sorbents is obviously a complex process, and there is considerable need to develop more accurate models involving sampling parameters that are of interest in actual field use.

An alternate method of concentrating organic gases is to condense the gases into a liquid phase with cryogenic sampling. No organic substrates are required. The low temperatures reduce unwanted reactions and artifacts. However, this technique needs to be evaluated to verify that the gases of interest are collected efficiently and that the water vapor in the sampled air does not block sampling lines. Additionally, an automated cryogenic sampling and analysis system that can be used in the field should be developed.

Analysis. Gas chromatographic separation of collected samples with mass spectrometric analysis of separated components (GC/MS) is presently the most popular technique for determining organic gases in ambient air. The equipment is relatively expensive, and highly trained operators are required. Fundamental information needs to be collected on the sampling and analysis system. For example, more complete data on GC retention times and mass spectral fragmentation patterns for organic compounds of interest need to be collected and cataloged in appropriate data systems. More software systems for data file searching and compound identification should be developed. Instrument manufacturers need to be involved in the development of standardized sampling, analysis, and data-handling equipment. This would simplify the transfer of GC/MS technology to the air pollution monitoring community.

An alternative system for the analysis of gaseous organic compounds consists of nondestructive and destructive detectors coupled in series with a GC. This system would be more economical than a mass spectrometer and could be easily used in the field. Types of detector pairs might include electron capture (EC)/photoionization (PI), or, with sample concentration, PI/FID, EC/FID, EC/IR (infrared), and PI/IR. With the information from the detector pairs and dual column retention times, it should be possible to make less ambiguous qualitative identifications.

No one analytical technique is ideal for all organic compounds. Therefore, newer technqiues, such as mass spectrometry-mass spectrometry (MS/MS), tunable atomic line molecular spectroscopy (TALMS), Fourier transform infrared spectroscopy, and newer gas chromatographic detectors,

Neighborhood monitoring station *includes a hi-vol sampler to measure particulate matter.*

need to be evaluated for environmental applications. Particularly interesting and potentially useful are combinations such as GC–FTIR–MS, which provide information not available with either technique alone. Our previous comments about using chemometric techniques to analyze data for organic particulate matter apply equally to data for organic gases.

Because there are hundreds of organic compounds of interest in the ambient air, it is not practical to attempt to develop methods for each individual compound. Screening techniques for classes of organic gases are greatly needed. These would help answer the questions of how extensive a problem is and what type of in-depth monitoring is required. Direct continuous monitors should be invented for chlorinated hydrocarbons such as carbon tetrachloride, chloroform, dichloroethane and tetrachloroethylene, benzene, toluene, and freons. Continuous monitors are also required for classes of compounds such as chlorinated hydrocarbons, aromatic hydrocarbons, and aldehydes. In both cases, FTIR and/or GC with EC/PI detection are prime candidates as analytical techniques. However, with FTIR, a concentration step may be required.

A serious problem requiring immediate attention is the lack of calibration methods and standards for organic gases at the low concentrations (ppt to a few ppb) at which measurements are made. No measurement method is complete until proper calibration standards are available, and at present the available standards are inadequate. Audit systems and devices that can generate known concentrations of organic gases at the ppt to ppb levels do not exist. The production of valid data for organic gases in ambient air will not be accomplished until these systems or devices are available. Having proper calibration standards for methods development is equally applicable to all areas addressed in this paper.

Source problems

Inorganic particulate matter. *Sampling and analysis.* Until now, NSPS regulations focused on reducing the levels of specific pollutants in stack emissions through the installation of best available control technology. In developing the NSPS, little attention was given to the impact of the NSPS on air quality itself; that is, secondary reactions such as agglomeration, condensation, chemical reactions, and size of the particulate emitted were not considered. However, because each NSPS eventually requires a State Implementation Plan (SIP) revision that focuses on air quality effects, secondary reactions and particle size are addressed here. The improvements in pollution control technology and the process changes mandated by NSPS regulations have significantly increased the relative contribution that condensible and fine particle emissions in the respirable range make to the total amount of particulates emitted from all sources. The impact of this increased contribution is magnified because in general more efficient control systems have resulted in lower particulate emission limits. EPA enforcement is now encountering the issue of fine particulates more frequently as it attempts to enforce EPA-approved SIP regulations that require measurement of particle size and noncondensible and condensible particulates.

Because of the emphasis now being placed on respirable-size particulates and fugitive particulate emissions, there is an urgent need to validate and standardize particle size sampling equipment in relation to design, operation, and interpretation of the results.

Particle size measurements on the same stack by different particle-sizing equipment (impactors, cyclones, etc.) frequently are not directly comparable because of differences in sampling rate, design, collection substrate, material, and orientation of the sampler. Also, the ancillary measurements needed to interpret the data, such as velocity, control device efficiency, temperature, moisture, and molecular weight of the stack gas, are not routinely recorded. Work was initiated in this area in 1982.

Test methods are needed for sources that have significant emissions of condensible particulates, such as ammonium compounds and acid mist, so that the impact of condensible particulates on air quality can be more accurately predicted and controlled where necessary. Test methods also need to be developed to allow the collection of a particulate sample that accurately represents both the particle size distribution in the stack and its impact on air quality.

A test method that discriminates between primary and secondary particulate sulfate in emissions from scrubber-equipped sources is also required as is a validated method for measuring the particulate matter downstream of a scrubber. Presently, particulate matter is measured upstream of a scrubber to avoid condensation reactions and entrainment of salts from the scrubber liquor. The effects of sampling equipment design, materials, temperature, and other parameters on this measurement need to be investigated.

A method to continuously and accurately monitor particulate emissions from stationary sources in general is needed.

As mentioned earlier, it would be desirable to utilize the present state of the art in source methodology and pollution control technology to simplify and refine the existing test methods to reflect process changes and technological advances. Any test method that is present in five or more SIPs should be considered for validation. Perhaps, specifications for equipment design, operation, and maintenance will be sufficient.

Enforcement of particulate emission regulations would be facilitated if reliable correlations could be made between plume opacity (visible emission mesurements), transmissometer readings, and mass emissions as measured by the manual particulate method. Condensation reactions, agglomeration, particle size changes, and analogous processes that occur in the stack gas between the points where the particulate sample and the transmissometer reading are taken, along with changes that occur between these measurement points and the stack exit, have prohibited these types of correlations, even on a source-by-source basis. Some of the problems cited earlier also affect this problem; test methods need to be developed to measure particle size and condensible particulate matter as an integral part of solving these problems.

A method to continuously and accurately monitor particulate emissions from stationary sources in general is needed. Possibly an in-stack optical technique such as an opacity monitor can be employed to meet this need. A method to measure particulate emissions where the particulate concentration changes rapidly is also required.

A means to assess the cause, scope, and magnitude of residual high-opacity plumes that appear at well-controlled sources, such as boilers and cement plants, is needed so that a strategy for reducing these residual plumes can be developed.

Methods to measure fugitive emissions are also required. As the major industrial sources of particulate emissions are controlled, the impact of these fugitive emissions on air quality will become more significant.

Also needed is a test method that collects a representative sample of asbestos (for example, particle size) as it exits the stack. At the same time the sampling problems are being resolved, a method that accurately measures the asbestos collected should be developed.

Much work should be done on the sampling and analysis of trace metals from incineration, power generation, and smelting sources. The only validated test method for trace elements is EPA Method 12, a method for lead. As in the ambient air methods, there is a question about the effectiveness of the present chemical extraction techniques for removing some of the trace metals from particulate matter.

Inorganic gases. *Sampling and analysis.* Sampling techniques that collect SO_3, H_2SO_4, HCl, HF, and other acid gases in a manner that represents their physical and chemical state in the stack must be developed if the emissions of these gases are to be accurately monitored on a continuous or intermittent basis. The current manual methods are nonspecific—that is, SO_3 cannot be clearly discriminated from H_2SO_4, and hydrogen chloride gas cannot be discriminated from hydrochloric acid. Without accurate manual methods, continuous monitors for these pollutants cannot be certified for accuracy.

A manual test method for NO_x that does not rely on grab samples and does not suffer interference from chloride is presently under development in EMSL/RTP. This method may be used for accurately measuring the NO_x levels in stacks and for validating continuous NO_x monitors. For those times when a continuous emission monitor (CEM) fails or is not available for the specific application, manual sampling methods need to be developed and validated that will supply accurate 24-h averages for NO_x and SO_2.

Fuel sampling and analysis for sulfur content as an alternate means of determining compliance with SO_2 emission rates needs to be tested through long-term field studies in which the fuel sampling and analysis results are statistically compared to the SO_2 concentrations in the stack as measured by a CEM. The impact of the fuel sampling technique (frequency, size of sample) on the fuel analysis results must be studied to allow the accuracy of the sulfur content to be reliably predicted.

Test methods to simultaneously measure CO_2, SO_2, SO_3, and particulate emissions are being considered or have been proposed by EPA but have not been validated.

Alternate methods for determining compliance, such as portable monitors that can be used in place of the present wet chemical methods, need to be developed and validated. These monitors could serve as inexpensive screening techniques that could be used to determine if a complete compliance test needs to be done. They could also serve to alert the plant operator to malfunctions in the process or deterioration of the control devices.

Alternate analytical methods for NO_3^-, SO_4^{2-}, CO, H_2S, etc., which reflect improvements in the state of the art, are needed. Many of the present wet chemical methods, although accurate, employ techniques that are infrequently used in the modern laboratory.

Organic particulate matter. *Sampling and analysis.* Very little work has been done on the development of methods suitable for collecting and analyzing stable and representative samples of organic particulate matter. The pollutants in question include oils, solids, and materials adsorbed on inorganic particles or contained in carbonaceous soot. Organic solids often have significantly large vapor pressures, and when gas is passed over particles collected on a filter, this may cause enough evaporation to require the use of a backup system. In some instances, special sampling methods will be required that will not disturb the true sample composition. Examples of these pollutants include polycylic aromatic hydrocarbons, heterocyclics, and PCBs.

Sampling and analysis for nontoxic, nonvolatile solids will probably require standard Method 5 techniques, involving only field validation. Analysis of toxic organics is more involved.

Techniques must be developed to separate and identify the materials in question, which are often chemically similar. Such work may require advanced techniques such as GC/MS and the characterization of a series of compounds. These procedures would also be used to determine if sampling methods have disturbed the relative concentrations of the series. When methods are likely to be employed by a large number of source samplers, studies should be initiated to simplify and reduce the cost of analysis.

Interest has been expressed in the development of automatic instruments for the measurement of benzo[*a*]pyrene and, perhaps, other polyaromatic hydrocarbons as well. There has been a lack of research in this area, and at the least, a feasibility study should be conducted.

Organic gases. *Sampling.* Integrated bag sampling and the methods involving solid absorbents are largely employed in sampling for nonreactive organic gases. These techniques have been studied thoroughly and require little additional research. In the development of future methods, the only parameters that need to be determined are those dealing with specific compounds of interest. On the other hand, some very reactive organic pollutants need special sampling methods, often including conversion to a derivative suitable for use in subsequent analysis. Important sampling problems exist in the development of methods for total nonmethane organic emissions. Losses of sample by adsorption on sample lines or by decomposition cause serious errors in this type of analysis and require further investigation. Such problems are often source-specific and have to be solved on a case-by-case basis.

Sampling problems are also prevalent in the use of continuous emission monitors. In addition to source-specific problems, questions are often raised when monitoring data obtained at particular points in time are compared with the time-integrated values obtained with manual compliance methods. There is a need for gas-collecting devices that produce information that is averaged over time.

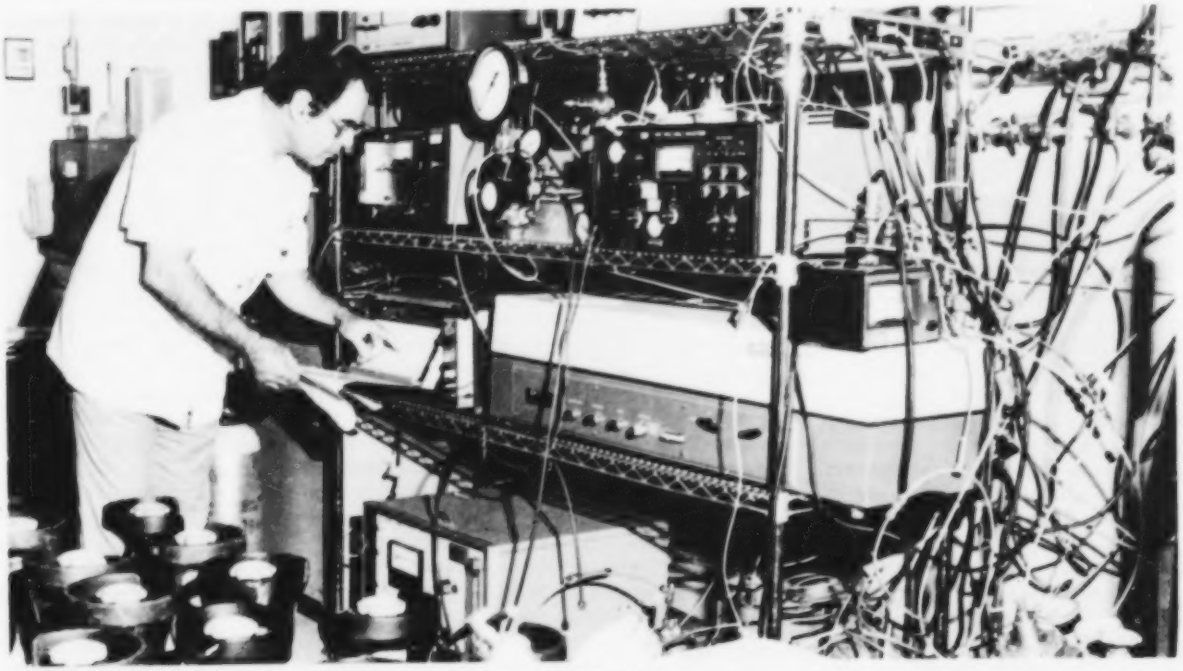
To ensure compliance with EPA regulations, it is essential to develop test methods for organic gases emitted from stationary sources. Many new test methods are required for organic pollutants, while some existing techniques need to be improved. It is important to develop sampling methods that consider the reactivity of the compounds being measured.

Many organics are so stable that integrated samples can be safely stored in the gas phase or on simple absorber materials prior to analysis. It may be possible to design generalized test methods that would require validation only for specific compounds.

Reactive organics should be collected in a medium that forms a stable reaction product that is unique for the substance under analysis. Specialized test methods must be designed for each such reactive organic material. Specific methods are needed for determining: acrylonitrile emissions from manufacturing and fiber production facilities; formaldehyde from phenol/formaldehyde processes and incinerators; ethylene oxide; nitrosamines; and total aldehydes.

Some sampling problems result from the nature of the source, rather than from the chemistry of the pollutants. For example, fugitive emissions cannot be measured correctly with hand-held monitors. Regulatory considerations also necessitate the development of sampling procedures, especially 24-h sampling methods, to use intermittently if the continuous monitor fails. Adapting generalized methods for organics to 24-h sampling would be a valuable achievement.

Although our primary emphasis will remain oriented toward meeting the methodology requirements of 40 CFR, parts 60 (NSPS) and 61 (NESHAP), test methods of known precision and accuracy are needed for determining the DRE (destruction and removal efficiency) of waste incinerators for Part 261—Appendix VIII materials. Accurate and precise methods are required because the issuance of an operating permit for routine disposal of these wastes may be based on a single trial burn. If the test method is not quantitative, an inadequately designed or operated incinerator that could



Analytical instruments *used to analyze air contaminants in the laboratory*

Some sampling problems result from the nature of the source, rather than from the chemistry of the pollutants.

endanger public health might be certified. On the other hand, an inaccurate or imprecise method could cause an adequately designed incinerator to fail the DRE test, causing economic loss to the owner of the facility and further compounding the already difficult problems associated with disposal of hazardous wastes.

Research into new technologies for sampling and analysis may be very fruitful. For example, valuable results could come from the development of simple, inexpensive methods for polychlorinated dibenzodioxins. Other important chemical studies would involve designing an automatic monitor for formaldehyde and instruments that measure organic emissions from flares. Remote sensing for organics using LIDAR or LOPAIR are also important areas for study.

Analysis. Because source measurements usually involve relatively high concentrations of pollutants, detection difficulties are rarely encountered. Separating interfering substances from the compounds of interest causes the more common problems. For stable organics, GC/FID is generally the method of choice. Research is needed on methods for polychlorinated dibenzodioxins and polychlorinated phenols. EPA Method 25 is of growing importance for measuring many types of emissions from the manufacture of synthetic organic chemicals. Studies are needed to refine Method 25, to compare it with alternate methods, and, when it has been validated, to collaboratively test it.

Developing automatic monitors involves analytical problems of varying levels of difficulty. There are process monitors for many stable organics, which can be adapted to emission measurements, and there is a recognized need for emission monitors. Monitors for benzene, vinyl chloride, and chlorinated hydrocarbons are urgently required.

Also needed are screening devices to determine concentrations of pollutants around chemical plants or hazardous waste disposal sites. In addition, inspectors need methods to determine if compliance testing should be performed.

Physical parameters. *Sampling and analysis.* In addition to the pollutant concentration measurements required under the NSPS and NESHAP regulations, other ancillary measurements, such as stack gas velocity, process rate, gas temperature, and moisture content, are necessary to derive a pollutant emission rate in terms of the applicable emission standard. Measuring these parameters becomes difficult or impossible under nonideal sampling conditions with a correspondingly adverse effect on the determination of the pollutant emission rate. Research programs are therefore needed to address these problems.

Most emission standards are expressed in terms of some parameter that relates to the process, such as pounds of pollutant per ton of manufactured product. Obviously, how accurately the process parameters are estimated directly affects the accuracy of the estimated pollutant emission rates. Here the error in the measured emission rate can be high because it is difficult to verify plant production rates. This is one of the most critical areas where further research is needed.

To reduce sampling costs, it is important to develop simplified methods for sampling stacks with standard configurations. For example, studies need to be done to determine if the number of sampling points per test can be decreased without affecting the accuracy of the test.

Although conventional sources present many sampling problems, nonconventional sources, such as variable batch processes, those with fugitive emissions from leaks or storage piles, and sources with roof or vent discharges, present special sampling problems that need to be addressed.

Most plants routinely monitor the operation of their control devices through some physical measurement such as scrubber or baghouse pressure drop, ESP voltage, or the energy use of the control device. Studies should be designed to determine if these measurements can serve as a means of estimating compliance in lieu of continuous stack monitors or 24-h sampling methods.

The effect that a low Reynolds number has on the accuracy of Pitot tubes also should be evaluated in depth. In addition, the need to sample isokinetically in all particulate tests should be studied.

Exposure monitoring problems

Inorganic particulates. Inexpensive and reliable devices to monitor particulate matter in ambient, indoor, or microenvironment exposures are increasingly needed. Two monitors capable of collecting particulates for later chemical analysis are available. Harvard University developed one that uses a 37-mm Fluoropore filter and cuts at 10 μm and 3.5 μm, and the National Bureau of Standards (for EPA) developed the other, which uses a Teflon and Nuclepore filter and cuts at 10 μm and 3.5 μm. Neither monitor has been thoroughly evaluated.

A portable instrument capable of giving real-time measures of particulate matter is the Thermo Systems Incorporated (TSI) Piezobalance; it employs the piezoelectric principle to measure the mass of particles smaller than 3.5 μm that impact on a quartz crystal through electrostatic precipitation. Another portable instrument is the GCA Respirable Aerosol Monitor, which employs light scattering to give a continuous readout of particle mass. Both of these instruments require much more evaluation before they can be used in a major exposure study.

To overcome the excessive noise associated with ambient particulate monitors for exposure studies, modifications have been made to reduce the air flow. However, before such monitors are put into widespread use, a major development effort must be undertaken to address the specific problems associated with monitoring indoor environments. Once a system is adequately designed, it can be properly evaluated. Even though EPA is not directly involved in regulations pertaining to indoor air pollution, any study that involves either the direct measurement of personal exposure or indirect techniques for calculating personal exposure will require the monitoring of indoor concentrations.

Particulate matter collected on fil-

ters of personal exposure monitors has been analyzed very little. Samples collected by the Harvard sampler have been analyzed for metals by X-ray fluorescence. Other analytical techniques are possible, but little information is available to determine the accuracy, precision, and other characteristics of the monitors. Further research is needed.

Inorganic gases. Active and/or passive devices exist for measuring personal exposure to carbon monoxide, nitrogen dioxide, and sulfur dioxide. A personal ozone monitor is not presently available, nor is there a very large need for such a monitor. Because most studies indicate that indoor SO_2 levels are lower than ambient levels, there is also very little need to improve the limits of detection and sensitivity of the existing instruments (impingers, molecular sieves, bubblers, and passive badges). Additional work is warranted, however, to reduce the size and improve the data management of CO detectors and NO_2 passive devices (Palmes tube, West permeable membranes, and NBS modified membranes). Field evaluation of the NBS modified membrane seems especially important for measurement of short-term (1–8 h) exposures to ambient levels of NO_2.

Organic particulate matter. Over the past several years, major advances have been made in the application of analytical techniques for the determination of organic particulate matter in samples of particulate matter. In general, these techniques require extracting the particulate matter and then applying an analytical method such as room temperature phosphorescence, synchronous luminescence, GC, HPLC, and TLC. Once the limitations of these techniques are known and overcome (or quantified), they can be successfully applied to the analysis of filters from the Harvard sampler or the NBS sampler. Proper attention must be devoted to the form of the particulate matter and the effects of sampling, collection, storage, and extraction on the reported concentrations. These limitations apply equally to the personal monitor and the indoor sampler.

Organic gases. Two types of devices have been used to monitor personal exposure to organic gases, and there are problems with both types. The active type draws air through a substrate using a portable pump. The passive type relies on gaseous diffusion principles to collect the sample. Tenax sampling with GC/MS analysis has been the most widely used active system to monitor personal exposure to organic gases. Existing information indicates that, even with proper care and attention, results obtained from the Tenax GC/MS system may be reproducible to only ±100%.

All of the sampling and analytical problems discussed in the ambient section apply to personal monitors. An additional problem associated with personal exposure monitors is that their small size limits the quantity of sample collected, so that detection limits are often inadequate. Passive devices using charcoal collectors for measuring organic gases in the ambient air presently suffer problems associated with high blank concentrations, which may be variable from badge to badge, and the problem of collecting enough samples for analysis during a short time period.

Summary

We have presented the many problems that EPA faces in developing methods to analyze for air pollutants. We have done so in the hope of stimulating the scientific community to develop new or improved analytical techniques to assist us in answering the myriad questions facing the regulatory community. We solicit your comments on this article and encourage your active participation in EPA's Research Grants Program.

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Mention of trade names or commercial products does not constitute endorsement or recommendation for use. In addition, any policy issues discussed in the paper should not be construed to represent official EPA policy.

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